

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 236 753 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.09.2002 Bulletin 2002/36

(51) Int Cl.7: **C08G 63/08, C08G 63/78,
C08L 67/04, C08L 67/02**

(21) Application number: **01200800.9**

(22) Date of filing: **02.03.2001**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: **Hycail B.V.**
9804 TG Noordhorn (NL)

(72) Inventors:
• **Lewis, David Neal**
9883 SL Oldenhove (NL)

- **Schutte, Gerrit**
7773 AL Hardenberg (NL)
- **Westerhof, Henk**
8406 AD Tijnje (NL)
- **Janssen, Jane**
7827 TL Emmen (NL)
- **Kelly, William E.**
9761 LJ Eelde (NL)

(74) Representative: **Prins, Adrianus Willem et al**
Vereenigde,
Nieuwe Parklaan 97
2587 BN Den Haag (NL)

(54) **Environmentally degradable polymeric compounds, their preparation and use as hot melt adhesive**

(57) The invention is directed to methods for preparing environmentally degradable polymeric compounds as well as to these compounds per se and to their use. The compounds of the present invention are comprised of a polycondensated lactic acid containing polymer, having a molecular weight (Mw) of from 500 to 50 000 g/mol, to which a flexibilizing aliphatic polyester having

a molecular weight of from 500 to 50 000 g/mol is coupled. The amount of lactic acid comprising groups in the polymeric compound ranges from 50 to 99% and the amount of flexibilizing polyester groups ranges from 1 to 50%.

EP 1 236 753 A1

Description

[0001] The invention is directed to environmentally degradable polymeric compounds as well as to methods for preparing these compounds and to their use.

[0002] Hot melt adhesives and coatings are used for a wide variety of commercial applications. The primary advantage of hot melt adhesive and coating systems is these systems require no carrier fluid or solvent for application to a substrate and, as a consequence, the need for subsequent evaporation of solvent or carrier fluid is eliminated. The lack of a drying or evaporation step allows these hot melt adhesive and coating systems to eliminate the hazards associated with use of solvents and the environmental impact of volatile organic compounds (VOC). Hot melt adhesive formulations can be varied over a wide range of adhesive properties from pressure sensitive to non-pressure sensitive in character. Pressure sensitive adhesives are used in applications where room temperature tack and long open times are required. Examples of such applications are adhesive tapes, disposable products like diapers, sanitary and incontinence pads. Non-pressure sensitive hot melts are used in applications like carton sealing, paper bag end sealing, telephone book and catalogue book-binding. Hot melt coating applications would include food trays, deli trays, disposable paper carton containers or other containers where a gross barrier would be needed.

[0003] Hot melt adhesives and coatings have typically been based on petroleum based polymers. Thermoplastic elastomers are used as the polymer component in the hot melt adhesives, which generally fall into three types: 1. petroleum based polymers such as polyethylene, polypropylene, ethylene-vinyl acetate, styrene block copolymers (e.g. styrene isoprene styrene, styrene butadiene styrene); 2. polyurethanes; and 3. polyester/polycarbonate materials.

[0004] These commercially available thermoplastic elastomers have certain drawbacks in their properties and manufacturing. The styrenic block copolymers are usually made by ionic polymerization that require the exclusion of oxygen and moisture of the system. The viscosity is high and the softening point is low. The polyurethanes are not thermally stable. Polyester must be synthesized under high temperature and vacuum. Moreover, they are very resistant to degradation. Recently, biodegradable hot melt adhesives were developed. Usually, hot melt adhesives are formulations containing base resins combined with plasticizers, tackifiers and other additives in order to reach diversified adhesive properties. In typical hot melt formulations, tackifier agents, plasticizers, and extenders like waxes are used to vary adhesion and flow characteristics. These products have the disadvantage of poor environmental degradability.

[0005] There is a strong need for packaging materials in which renewable resource materials like paper, starch, and certain degradable plastics (aliphatic polyesters, polylactides, etc.) are used. In the case of paper products, use of environmentally degradable (i.e. compostable or biodegradable) adhesives would allow composting of the glue or coating residue, when the paper or cardboard product is recycled. Or alternatively, composting of the entire paper product, unlike those coated or sealed with typical petroleum based hot melt formulations.

[0006] The term "environmentally degradable" as used herein, refers to products which are compostable and/or biodegradable, as is reflected by a substantial loss of mechanical properties (tensile strength, elongation to break, toughness) or structural integrity (breaks into small pieces) upon contact with moisture at ambient or elevated temperature conditions (for example, in a composting operation) during a prolonged period, i.e. typically more than one month. This loss of mechanical properties leads to complete degradation of the environmentally degradable product when it is subjected to the above-mentioned conditions during a period of typically two years.

[0007] It is an object of the present invention to provide a material that is environmentally degradable and that may be used as a melt adhesive, as a coating, as a castable film and/or as fibers.

[0008] In the art, several methods are known for providing environmentally degradable polymers. Patent publications WO-A-94/10257, US-A-5 252 646, and US-A-5 312 850 disclose compositions comprising 20 wt.% to 98 wt.% of a polylactide (PLA) homo- or copolymer containing at least 20 molar percent of the lactide component; 2 to 80 wt.% of a polar tackifier having a Ring and Ball softening point (as described by ASTM E-26) greater than 60°C; 0 to 50 wt.% of a plasticizer; 0 to 30 wt.% of a wax diluent; 0 to 3 wt.% of a stabilizer; and 0-20 wt.% of a polymer. The last component could be certain hydrophilic polymers such as starch, polyvinyl alcohol, hydroxyethyl cellulose, polyvinyl methyl ether, poly (ethylene oxide), or poly (hydroxybutyrate/hydroxyvalerate), which will function to increase the water sensitivity of the adhesives. Alternatively, it could also be a kind of thermoplastic polymer such as ethylene vinyl acetate, ethylene acrylic acid, ethylene methyl acrylate and ethylene n-butyl acrylate copolymers as well as caprolactone polymers to impart flexibility, toughness and strength. These methods use polylactides or polylactic acid polymers synthesized from lactide. Lactide is a cyclic diester obtained from the intermolecular coupling of two lactic acid molecules. The process for producing and purifying lactide and subsequent polymerization of lactide to make a polylactide is expensive and often cumbersome.

[0009] Several other publications are known in which polylactic acids are used as a component in biodegradable hot melt formulation or in an adhesive film formulation. However, these hot melt or adhesive film formulations have used polylactides or polylactic acid polymers synthesized by ring opening polymerization of lactide. As stated previously, this process for making polylactide is expensive and cumbersome.

[0010] Other biodegradable hot melt adhesive formulations are known from US-A-5 169 889 and EP-A-0 741 177.

These publications concern the use of the aliphatic polyesters polyhydroxybutyrate and polyhydroxypentanoic acid. These have generally been made by culturing specific bacteria, which incorporate these polyesters as an internal storage polyester. The process for isolating and purifying these aliphatic polyesters from the bacteria is expensive and time consuming. In most cases commercial production of these polyester by this route is economically not feasible.

[0011] However, the present inventors found that when pure lactic acid polycondensates reach a Mw of 3000-5000 g/mol they tend to stiffen. Unless indicated otherwise, the term "molecular weight" as used herein, refers to the weight average molecular weight (Mw) as measured for instance by gel permeation chromatography (GPC). Oligomers having a Mw higher than 3000-5000 g/mol may become very brittle. This is attributed to a glass transition temperature (Tg) that is too high. Moreover, the present inventors found that a lactic acid polycondensate starts to lose its surface tackiness at room temperature if polycondensate molecules reach a Mw above 3000 g/mol. The tackiness is totally gone at values of Mw above 10000 g/mol. These higher Mw polycondensates need to be in a molten state to display adhesion and to make them stick to metals, polymers, and paper.

[0012] It is an object of the present invention to provide for a compound which does not have the above-mentioned disadvantages, *i.e.* to provide for a compound that may be used as a hot melt adhesive which is environmentally degradable and which is more flexible than the prior art compounds. Also, such a compound should provide for an improvement in at least some of the other aspects that are important in environmentally degradable hot melt resins. These aspects include: open time (defined as the time in which the hot melt still retains its adhesive character. After this time, no substantial adhesion occurs), Tg (which should be decreased), and UV curability, when applicable. Also the compounds should be relatively easy to manufacture at a lower cost than prior art methods.

[0013] Surprisingly it was found that this object could be met by coupling aliphatic polyesters, such as polycaprolactone, to polycondensated lactic acid comprising chains, whereby the polyester groups act as a flexibilizing coupler or linker. Therefore, in a first embodiment, the present invention is directed to an environmentally degradable polymeric compound, suitable for use as a hot melt base resin, which compound comprises 50 to 99 wt.% polylactic acid comprising chains, each of said chains having a Mw of from 500 to 50 000 g/mol, to which chains a flexibilizing aliphatic polyester having a Mw of from 200 to 50 000 g/mol, is coupled, wherein the amount of aliphatic polyester in the compound is 1 to 50 wt.%.

[0014] Without wishing to be bound by theory, it is believed that the polyester species act as flexibilizing linkers or couplers between polycondensated lactic acid groups. This solves the problem of the brittleness, which is associated with pure lactic acid oligomers. The compound of the invention may, for example, be in the shape of a star having a core of polyester moiety at the core, while the arms are formed by the lactic acid oligomers. Alternatively, the compound may be in the form of a partial network containing polyester stars connected by lactic acid chains.

[0015] The molecular weight, Mw, of the aliphatic polyester, is according to the present invention from 200 to 50 000 g/mol. Values above 50 000 g/mol are generally too viscous to be mixed properly and, as a result, can usually not provide sufficient coupling sites. Polyesters having molecular weights below 200 g/mol are generally too small to provide adequate flexibility to the final compound. Preferably the Mw of the aliphatic polyester is from 1000 to 10 000 g/mol.

[0016] The polylactic acid comprising groups (or chains) may according to the present invention contain fragments derived from other monomers as well. For example the chains may contain other polycondensable combinations of L-lactic acid with D-lactic acid or with D,L-lactic acid or any other hydroxycarboxylic acid, such as glycolic, hydroxycaproic, hydroxyl valeric, etc, or combinations with diols, polyols (triols, tetrols, hexols, *etc.*) polymer diols, diacids, di, tri or tetra anhydrides or polyanhydrides, or aliphatic polyesters, *etc.* However, the majority of these groups, *i.e.* at least 75 and preferably at least 95 mol%, should be derived from lactic acid. Most preferably, however, these groups consist essentially of polylactic acid. The Mw of the polylactic acid comprising groups should be from 500 to 50 000 g/mol. Again, values above 50 000 g/mol are generally too viscous to be mixed properly and, as a result, can usually not provide sufficient coupling sites. Polylactic acid chains having Mw values below 500 g/mol will result in a system requiring an extensive polycondensation time to reach acceptable properties. Preferably the Mw of the polylactic acid comprising groups is from 1500 to 10 000 g/mol. The polylactic acid comprising groups should be present in the compounds of the invention in an amount of from 50 to 99 wt.%.

[0017] Suitable aliphatic polyester are functionalized polycaprolactones, in particular polycaprolactone polyols (diols, triols, tetrol or higher).

[0018] The flexibilizing aliphatic polyester may be a polymer or copolymer of hydroxycarboxylic acids, which is optionally substituted with hydroxy groups. Preferred compounds are polycaprolactone diol, polycaprolactone triol and polycaprolactone tetrol.

[0019] Hot melt base resins of the current invention may be produced by controlled polycondensation of L-lactic acid, D-lactic acid or D,L lactic acid (also known as 2-hydroxypropanoic acid) in the presence or absence of a catalyst followed by a condensation coupling reaction with the aliphatic polyesters to produce hot melts base resins with the desired flowability or viscosity, flexibility, pot life, open or setting time, tensile strength and extensibility.

[0020] The hot melt base resins of the present invention may also include any polycondensable combinations of L-lactic acid with D-lactic acid or with D,L-lactic acid or any other hydroxycarboxylic acid (glycolic, hydroxycaproic, hy-

droxylvaleric, etc) or combinations with diols, polyols (triols, tetrols, hexols, etc) polymer diols, diacids, di, tri or tetra anhydrides or polyanhydrides, or aliphatic polyesters.

[0021] The polycondensed polymer of the present invention may be prepared without catalyst in the presence of heat and sufficient vacuum or in the catalysts which promote esterification or transesterification. This type of reaction is carried out relatively more simply than ring-opening polymerization.

[0022] Suitable catalysts for this purpose are conventional transesterification catalysts, which comprise tin(II), tin(IV), iron(II), iron(III), zinc, calcium and/or magnesium metals; for example stannous oxide, stannous chloride, stannous bis 2-ethyl hexanoate (also known as stannous octoate), stannous acetate, stannous acetylacetonate, stannous lactate and zinc salts like zinc stearate, zinc oxide, zinc chloride, zinc lactate, iron (III) salts like ferric acetate and ferric lactate, etc. Preferred catalysts are stannous oxide and stannous chloride. Other suitable catalysts for this purpose are transition metal catalysts: e.g. aluminum, iridium, titanium, nickel, chromium, vanadium, hafnium, manganese, tungsten, tantalum, platinum, palladium, samarium, gallium, germanium, indium, cobalt, rhodium, rhenium, ruthenium, thallium, bismuth, cadmium, thorium and/or zirconium comprising compounds, which may be used in combination with the above-mentioned conventional transesterification catalysts. Also suitable are rare earth catalysts: e.g. europium, yttrium, erbium, dysprosium, holmium, neodymium, gadolinium, lutetium, lanthanum, praseodymium, terbium, thulium and/or ytterbium comprising compounds, which may also be used in combination with the above-mentioned conventional transesterification catalysts or transition metal catalysts.

[0023] The above-mentioned catalysts may also be used in combination with acidic catalysts, such as sulfuric acid, phosphoric acid, hydrochloric acid, methanesulfonic acid, toluene sulfonic acid.

[0024] The preparation may be carried out using conventional polymerization and polycondensation techniques.

[0025] The synthesis may be carried out using a two step route, in which in Step 1 the polylactic acid comprising groups are synthesized by polymerization. A catalyst may be used to decrease the reaction time. A low Mw acid or alcohol may be used as an initiator for the polycondensation, in which case a carboxylic or hydroxyl functional product is formed, rather than a bi-functional product. Other hydroxyacids then lactic acid can be used for copolymerisation as well. According to the invention a lactic acid based copolymer is obtained, having a Mw in the range of 500 to 50 000 g/mol.

[0026] Suitable reaction conditions for this first step comprise a temperature of from 150 to 260°C preferably from 180 to 200 °C, and a reaction time of 1 h to more than 20 h. The synthesis is preferably carried out in vacuum, preferably less than 15 mbar, dependent upon the amount of water present in the reaction mixture. Most preferred are pressures of 0 to 15 mbar.

[0027] Step 2 comprises the coupling of the polycondensated lactic acid oligomer made in step 1 with one or more "flexible" aliphatic polyester components by esterification and/or transesterification or via chain coupling with a chain coupling agent.

[0028] Low Mw components may also be used to change the hydroxyl/carboxyl (OH/COOH) ratio in order to attain a desired molecular weight or a desired functionality. Multifunctional components may also be used to obtain a specific functionality. In this way a flexible copolymer with a molecular weight of 500 to 100 000 g/mol may be obtained.

[0029] Suitable reaction conditions for Step 2 comprise a reaction temperature of 160 to 270°C, preferably of from 190 to 220°C, a reaction time from 0.2 to 10 h, while the reaction is preferably carried out in vacuum, preferably below 50 mbar, most preferably from 10 to 20 mbar.

[0030] A rotary evaporator or another standard polycondensation setup may be used to carry out both steps.

[0031] The preparation may also be carried out in a single step, viz. by combining Steps 1 and 2. In this case, the components mentioned above for Steps 1 and 2 are mixed. Then the reaction is carried out at a temperature of 160 to 270°C, preferably 190 to 220 °C, during 1 to more than 20 hours at a vacuum pressure of down to less than 15 mbar, depending on the amount of water present in the reaction-mixture, preferably 0 to 1 mbar. In this way, a flexible copolymer with a Mw weight (Mw) of from 700-200 000 g/mol may be obtained. The Mw of the polymeric compound of the invention is preferably from 700-100 000 g/mol, most preferably from 2000 to 50 000 g/mol.

[0032] Alternatively, the synthesis may be carried out in three steps, wherein Step 1 and 2, as described above, are followed by a Step 3, which comprises endcapping or chain extending of the polymers chain to improve the stability of the polymer, increase the molecular weight or to create different functionality or non-functionality.

[0033] L-Lactic acid, D-Lactic acid and DL Lactic acid may be used to prepare the polylactic acid comprising groups. Suitable polycondensation catalysts are the conventional catalyst used for this purpose, such as tin oxide, tin chloride, zinc stearate, toluene sulfonic acid (TSA), etc.

[0034] The aliphatic polyester, which is used as a "flexible component" may be polycaprolactone polyol (diol, triol or tetrol) with a Mw of 100 to 50 000 g/mol. The low molecular weight alcohols mentioned above may be selected from diols such as ethyleneglycol, propyleneglycol, butanediol, hexanediol, neopentylglycol, 1,4 dimethylolcyclohexane, 2,2,4-trimethylpentanediol-1,3, 1,3-butanediol, etc.; triols such as trimethylolpropane, trimethylolethane, etc.; and polyols such as pentaerythritol, dipentaerythritol, etc.

[0035] The low molecular weight acids may be selected from dicarboxylic acids such as adipic acid, sebacic acid,

succinic anhydride, maleic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride, 1,4-cyclohexanedicarboxylic acid; phthalic anhydride isophthalic anhydride, *etc.*; and polycarboxylic acids such as trimellitic anhydride, pyromellitic dianhydride, *etc.*

[0036] Other low molecular weight single or multifunctional components that may be used are hydroxyacids such as dimethylolpropionic acid, *etc.*; lactones such as butyrolactone, ϵ -caprolactone, *etc.*; aminoacids; aminoalcohols such as taurine; hydroxysulfates; epoxies such as ethyleneoxide, propyleneoxide, Cardura E, glycidol; epoxyacrylics such as glycidylmethacrylate; and acetic anhydride

[0037] Chainextenders or crosslinkers that may be used in Step 3, mentioned above, are dianhydrides such as pyromellitic dianhydride; di- or tri-isocyanate such as hexamethylenediisocyanate, isophorone diisocyanate, isocyanurates, allofenates, *etc.*; diepoxies such as the diglycidylether of butanediol, the diglycidylether of bisphenol A, *etc.*; diamines such as hexanediamine, polyoxypropylenediamine, *etc.*; silanes; and peroxides such as benzoylperoxide, T-butyl peroxybenzoate, *etc.*

[0038] Polymers of the present invention produced in the initial polycondensation step have Mw values of between 500 and 50,000, preferably in the range of 1500 to 10,000. The polylactic acid comprising groups in the coupling step of the current invention can include other degradable aliphatic polyesters, such as polycaprolactones, polyester diols, polyester triols or polyester tetrols or polyester hexols either produced by polycondensation or by ring opening polymerization. These can include copolymers of lactide or glycolide and caprolactone or copolymers comprising other monomers, which may be subjected to ring-opening, such as valerolactone. The preferred coupling polymers are polycaprolactone diols, triols or tetrols, which provide flexibility, extensibility, and a glass transition temperature (Tg) below room temperature to the final hot melt base resin. The coupling reaction may include partial transesterification reactions to occur, particularly in the presence of a transesterification catalyst. The Mw of the coupling polymer can be in the range of 200 to 50,000, but preferably is in the range of 1000 to 10,000. The amount of coupling polymer in the final hot melt base resin varies between 1 to 50 %, preferably in the range of 10 to 30%.

[0039] The coupling of the polycondensed polymer of the first step and the polymer of the second step can alternatively be accomplished by the use of coupling agents including cyclic anhydrides, mono-, di-, tri- or tetracyclic anhydrides, polyanhydrides, cyclic or glycidal ethers, aliphatic isocyanates, aliphatic polyisocyanates, silanes and chlorosilanes. Hot melt base resins of the present invention can be made ultraviolet curable by use of double bond containing diol or diacid components. Properties of the hot melt base resins can be further modified by partial crosslinking with the use of organic peroxides like cumyl peroxide, tertbutyl peroxybenzoate, tertbutyl peroxyacetate, *etc.*

[0040] The hot melt base resin of the present invention can also be used as a thermoplastic elastomeric modifier for high molecular weight polylactide resins or glycolic acid-lactic acid copolymers which are normally hard, brittle polymers to improve flexibility and impact properties.

[0041] Other applications include hot-melt adhesives and coatings via hot spray, laminates, tie-layers, bonding materials, additive to other polymer system for applications too numerous to mention, fiber/filament applications, potential spun bonding or melt blown for fiber formation.

[0042] One of the important aspects of this invention is that the polymer has relatively high surface tension, which allows for printing - directly without surface treatment. The resulting material is hot water resistant and not solubilized by hot water.

[0043] The end use products which may be obtained in accordance with the present invention comprise carton sealing, book bindings, such as bindings of telephone books and catalogues, adhesive tapes, diapers, sanitary napkins, incontinence pads, disposable paper products like food trays, deli trays, carton containers or other products where a gross water barrier would be desired.

[0044] The invention will now be illustrated by the following, non-limiting, examples.

Example 1

[0045] 800g of 88% L-Lactic Acid (obtained from ADM) solution is placed with 1.6g (0.2 wt%) Tin (II) oxide (obtained from Acros) powder into a 1 dm³ pear shaped flask. The flask is attached to a rotary evaporator unit. An argon purge tube is mounted in the rotary evaporator unit so it rests just below the surface of the lactic acid solution in the flask. An oil bath is set to 180°C and raised until the pear shaped flask is partially immersed. The vacuum pump attached to the rotary evaporator unit is set to 800 mbar for 0.5 to 1 hour. The argon is bubbled through the lactic acid solution and the system maintained at 800 mbar vacuum and 180°C temperature until almost the Tin (II) oxide disappears. The liquid will change gradually from dark gray to a hazy clear solution. The vacuum is gradually increased over the next hour to 100 mbar and the argon also subsequently reduced. After this second hour, the argon flow is stopped and the vacuum increased (or pressure reduced) to the maximum amount (5-10 mbar) and the polycondensation reaction continued for 6 hours. After this time, the vacuum is released by increasing the flow of argon; increasing the vacuum control setting to atmospheric pressure, then the flask is removed and 96 g (12%) polycaprolactone tetrol (CAPA 205042, obtained from Solvay, having a number average molecular weight (Mn) as determined by end group analysis

of 8000 g/mol) is added to the pear shaped flask, after it is removed from the rotary evaporator unit. The vacuum is again set to its maximum value, the oil bath temperature raised to 195°C and the coupling reaction allowed to take place for 4 hours. The final product is a slightly yellow liquid, which upon cooling to room temperature is a slightly flexible solid and has a Mw of 17,400.

Example 2

[0046] Calculations in this example are based on the functional groups of the available raw material and will therefore change if different initiation cores are used. Two low Mw caprolactone species from Solvay were used; CAPA 316 (tetra-functional polyol, Mn 1000 g/mol, as determined by end group analysis) and CAPA 205042 (similar to CAPA 316 but with Mn 8000 g/mol).

[0047] The reaction ratio was based on the functional groups of the caprolactone segment (polyol). Complete reaction between the caprolactone segments and the lactic acid polycondensate segments was assumed. The molecular ratio between the tetra-functional CAPA 205042 (or CAPA 316) and a lactic acid polycondensate segment was 1:4, respectively. One part of a caprolactone segment can react with four parts of a lactic acid polycondensate segment.

[0048] At the beginning of each experiment a desired molecular weight is defined. Hereby the amount of lactic acid that is needed can be calculated, since the CAPA segment has a fixed molecular weight. For example, if the desired molecular weight of the end product is 28000 g/mol and if CAPA 205042 is used as the flexible segment, which has a Mw of 8000 g/mol, the residual Mw 20000 has to be lactic acid. For this molecular weight, approximately 20 000 / (90.04 - 18.02) = 288 coupled LA molecules are required. From this the amount of raw lactic acid could be calculated, based on the purity and concentration.

[0049] The following raw materials were used in this Example for the polycondensation synthesis:

- * CAPA 205042 (Solvay Interlox Ltd., development product, pentaerythritol initiated caprolactone Mw +/- 8000 g/mol)
- * D,L - lactic acid (lactic acid contained about 12% H₂O)
- * L - lactic acid (lactic acid contained about 12% H₂O), (ADM heat stable)
- * Tin-catalysts
- * Protonic acids

[0050] The following equipment was used in this Example:

- * Heidolph rotating evaporator
- * Heidolph MR2002 oil bath 50-350 °C + magnetic stirrer
- * Digital temperature sensor, Greisinger GTH 175/MO
- * Vacuum pump Welch mod 110 1007434
- * Vacuum regulator Leibold, Divatron DT1

[0051] The following analyses were carried out in this Example:

- * molecular weight analysis by GPC, Hewlett Packard 1100 Chemstation
- * thermoanalysis by DSC (T_g and T_m), Perkin Elmer Pyris1

Example 2.1

Introduction:

[0052] Polycondensation of L-lactic acid in the rotating evaporator was carried out without catalyst.

Raw materials:

[0053]

- * L-lactic acid

Process:

[0054] Polycondensation of L-lactic acid without catalyst

EP 1 236 753 A1

Reaction Time (min)	Temp oil (°C)	Press. (mbar)	Mw (g/mol)
125	113-121	300 +/- 5	
140	135-143	200	
80	151-163	200	
135	152-159	200	
340	177-182	200	2111
60	177-182	600	
240	177-182	200	
120	185-193	100	2797
240	183-189	100	
180	183-189	50	
14	183-189	40	5086

Results:

[0055] Hard and non-sticky polycondensate, white non-transparent (probably because of crystallization). Mw: 5086 g/mol.

Example 2.2

Introduction:

[0056] Esterification of L-lactic acid polycondensate with a molecular weight of approximately 5000 g/mol with CAPA 205042 in a rotating evaporator.

Raw materials:

[0057]

- * The L-lactic acid polycondensate (LA PC) from Example 2.1
- * CAPA 205042

Process:

[0058] Polycondensation in the rotating evaporator without adding catalyst.

CAPA205042:	20.23 g
LA PC:	51.90 g

Reaction Time (min)	Temp oil (°C)	Press. (mbar)
5	160-181	800 +/- 5
30	189-191	200
275	189-191	100
270	189-191	50

Results:

[0059] Material is solid and looks and feels waxy.

[0060] DSC analyses results:

$$T_g = -3.2 \text{ °C}$$

$T_{\text{crystallization}} = 81\text{ }^{\circ}\text{C}$

$T_{m1} = 108\text{ }^{\circ}\text{C}$

$T_{m2} = 124\text{ }^{\circ}\text{C}$

$T_{m3} = 133\text{ }^{\circ}\text{C}$

SEC analysis result:

$M_w = 10560\text{ g/mol}$

Example 2.3

Introduction:

[0061] L-lactic acid was polycondensated until all the free water was removed from lactic acid solution. After removing the water, CAPA 205042 was added to the flask. The esterification reaction was continued in order to obtain polymer with a flexible core, having a M_w of 50 000 g/mol.

Raw materials:

[0062]

- * The L-lactic acid polycondensate (LA PC) from Example 2.1
- * CAPA 205042

Process:

[0063] Polycondensation in the rotating evaporator without adding catalyst.

L-lactic acid	771.53 g
---------------	----------

Reaction Time (min)	Temp oil ($^{\circ}\text{C}$)	Press. (mbar)
30	600 +/-3	108
30	475	110
330	200	112

Results:

[0064] From the initial 771.53 g L-lactic acid, 124.88 g water was removed: $(124.88 / 771.53) * 100\% = 16.2\%$, indicating that lactic acid was already polycondensated.

Calculation of the amount CAPA needed:

[0065] The desired M_n is 50 000 g/mol. The CAPA segment have a M_n of 8000 g/mol the rest is Lactic acid so 42000 g/mol. The amount of CAPA needed: $(647/42000) * 8000 = 123\text{ g}$. Added:

CAPA 205042: 122.90 g

Reaction Time (min)	Temp oil ($^{\circ}\text{C}$)	Press. (mbar)
15	25-110	800 +/-3
40	110	800 \rightarrow 200
40	117	50
110	139	50
130	160	50
100	180	50

[0066] The polycondensate was opaque, slightly yellow, having little crystallinity. The polycondensate was sticky.

EP 1 236 753 A1

Reaction Time (min)	Temp oil (°C)	Press. (mbar)
60	178	800 → 70
180	189	70
220	190	200 + Argon flow

Results:

[0067] Mw after one day's reaction: 2500 g/mol. After 2 days it was 4700 g/mol. The material was slightly soft, but looked and felt waxy. This indicated that the material had different phases. Probably transesterification had taken place, because the molecular weight of the CAPA had decreased.

Example 2.4

Introduction:

[0068] In this example a paperboard coating was formed by esterification of L-lactic acid with CAPA205042.

Raw materials:

[0069]

- * L-lactic acid
- * CAPA 205042
- * Benzoyl peroxide

Process:

[0070]

L-lactic acid	861 g
---------------	-------

Reaction Time (min)	Temp (°C)	Press. (mbar)
30	100	800 +/- 5
150	105	600
15	110	400
75	115	300
40	116	200
70	142	200
235	149-155	200
110	167-173	200
170	176-184	200
270	176-184	200
210	176-184	100
60	176-184	50

[0071] 242 g water was withdrawn from the polycondensation. In the removed water, there was some lactic acid present, since the water had an odor of lactic acid. CAPA 205042 was dried in a rotary evaporator at 800 mbar and 130°C for 6 hours.

[0072] Further synthesis:

CAPA 205042: 80 g
L-lactic acid polycondensate (see above): 200 g

Reaction Time (min)	Temp (°C)	Press. (mbar)
30	133	800 +/- 5
45	144	800
15	154	500
30	156	200
260	175	200

Results:

[0073] After finishing the synthesis, the melt was applied to a piece of paperboard fruit tray with a brush. The coated tray did not feel sticky. The fruit tray was filled with water, which was left there for several hours. After removing the water the coating did not show any signs of being dissolved or softened by the water. In addition, the material was treated with 0.2 wt% of benzoyl peroxide in order to create entanglements between the molecular chains. Besides crosslinking, peroxides also act as a catalyst deactivator which enhances the stability of the polycondensate.

[0074] At first a small amount of peroxide was fed (while stirring) to the molten product at a temperature of 180°C. Regions of high cross-linking occurred because of the fast reaction of the peroxide (probably because of the high temperature). The temperature of the melt was lowered to approximately 125-130 °C and the rest of the peroxide was added. After the addition the melt was rotary evaporated to react for 120 minutes. The flexibility of the coating increased.

Example 2.5**Introduction:**

[0075] In this experiment L-lactic acid polycondensate together with the CAPA 205042 was polycondensated in the presence of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and TSA.

Raw materials:

- * L-lactic acid polycondensate ($M_w \sim 1200 \text{ g/mol}$)
- * CAPA 205042 ($M_n \sim 8000 \text{ g/mol}$)
- * $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
- * p-Toluene sulfonic acid mono hydrate 99% (TSA)

Process:

[0077] Step 1: polycondensation of L-lactic acid pre-polycondensate with 0.3 wt% $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.3 wt% TSA.

L-lactic acid polycon	589 g
$\text{SnCl}_2 \cdot \text{H}_2\text{O}$	1.8 g
TSA	1.8 g

[0078] Step 2: addition of CAPA 205042.

CAPA 205042	110.14 g
-------------	----------

Reaction Time (min)	Temp (°C)	Press. (mbar)
70	180	38 +/- 3
20	180	25
110.14 g of CAPA 205042 was added		
330	193	20
405	200	20

Results:

[0079] The polycondensate looked brownish. The material was very flexible, non-sticky and found to be water resistant. The material could be used as a flexible coating. Molecular weight analyses by GPC: Mw approximately 37000 g/mol (Dispersion = 5.7). DSC analyses: $T_g = -20\text{ }^{\circ}\text{C}$.

Example 2.6

[0080] In this experiment L-lactic acid was pre-polycondensated until all the free water was removed and the lactic acid was slightly polycondensated. Then CAPA 205042 was added to the lactic acid polycondensate and the reaction was continued for a certain period of time. In the last stage of the reaction $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and TSA were added.

Raw materials:

[0081]

- * L-lactic acid
- * CAPA 205042 ($M_n \sim 8000\text{ g/mol}$)
- * $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
- * p-Toluene sulfonic acid mono hydrate 99% (TSA)

Process:

[0082]

Stage 1) polycondensation of L-lactic acid

Stage 2) addition of CAPA 205042

Stage 3) addition of $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ and TSA

L-lactic acid after 1 stage	801.7 g
CAPA 205042	153.3 g
$\text{SnCl}_2 \cdot \text{H}_2\text{O}$	2.4 g
TSA	2.4 g

	Reaction Time (min)	Temp ($^{\circ}\text{C}$)	Press. (mbar)
Stage 1	105	132	600 +/- 3
	70	137	500
	25	139	400
	40	139	200
153.3 g of CAPA 205042 was added			
Stage 2	10	134	200 +/- 3
	35	153	200
	65	170	200
	40	180	100
	76	182	80
	24	184	40
	55	184	30
	75	199	30

EP 1 236 753 A1

(continued)

	Reaction Time (min)	Temp (°C)	Press. (mbar)
Temp set to 150 °C and Press.to 800 mbar. Then 2.4 g SnCl ₂ H ₂ O and 2.4 g TSA was added			
Stage 3	30	150	800 +/- 3
	80	180	800
	35	180	100
	85	180	50
	90	180	35
after 8 days	30	165-175	100 +/- 3
	50	192	35
	110	193	30
	260	193	25-30
after 9 days	90	193	25 +/-3
	75	193	20
	300	193	15

Results:

[0083] The colour of the polycondensate looked brownish. The product was very strong, flexible, not tacky and very good water resistant.

[0084] Analytical results:

Mw at the end of the stage 2	2200 g/mol.
Mw at the end of the stage 3	4648 g/mol
Mw after 8 days	15098 g/mol
Mw finished product	21740 g/mol

Example 3

[0085] Hot-melt glues were prepared along the lines indicated in the previous examples by using the following materials and procedures:

Ingredient	Amount	Procedure
L-lactic acid (88%)	800 g	Rotavaporator at 180 °C Stepwise reduction of the pressure to about 100 mbar for 6 hours Temp 195 ° C, p = 5 mbar; additional 4 hours
SnO	1.6 g (0.2 wt% of A)the lactic acid)	
CAPA 205042	96 g (12wt% of A)the lactic acid)	

[0086] Average properties of the glues were found to be:

Extensibility: > 500%
Open Time: > 40 s
Viscosity: ~1000 mPas
Weight loss stability (~160°C):

after 3 h	5 %
-----------	-----

(continued)

after 7 h	8 %
after 24 h	25 %

[0087] Additional glue formulations for hot-melt applications were prepared as described in Example 3. The molar mass and its distribution are given in the following table.

Example No.	Polycondensate			Glue		
	M_w /[g \cdot mol $^{-1}$]	M_n /[g \cdot mol $^{-1}$]	MWD	M_w /[g \cdot mol $^{-1}$]	M_n /[g \cdot mol $^{-1}$]	MWD
3-2	9 100	7 000	1.30	28 800	6 100	4.75
3-3	4 600	1 500	3.07	26 100	5 300	4.97
3-4	3 200	1 100	2.80	31 800	6 300	5.05
3-5	5 900	1 900	3.12	31 900	7 400	4.31
3-6	8 900	2 900	3.09	27 900	19 600	1.42

[0088] The thermal properties found using a Perkin-Elmer Pyris 1 DSC were as follows:

Example No.	T_g / °C	T_c / °C (DH / Jg $^{-1}$)	T_m / °C (DH / Jg $^{-1}$)
3-2	-14	94 (-9.6)	135 (10.7)
3-3	-12	82 (-21.3)	133 (22.9)
3-4	-9	95 (-2.8)	134 (6.0)
3-5	-22	84 (-12.7)	130 (15.0)
3-6	-	-	-

[0089] ^1H NMR analysis gave the following results:

Example No.	M_n^a (g/mol)	Lactide b (mol %)	CL c (mol %)
3-2		4.9	17.7
3-3	39 000	4.2	16.8
3-4	40 000	3.1	16.9
3-5	32 000	3.6	23.6
3-6	30 000	3.4	18.7

^a Based on end group analysis.

^b Note: 1 mol lactide = 2 mol lactic acid units in polymer.

^c Amount CL units vs. lactic acid units in the polymer.

[0090] Furthermore, the following average properties were found.

Weight loss stability (~ 170 °C): < 10% in 8 hours

Extensibility > 600 % for all samples

[0091] It was concluded that the above-mentioned properties of the compounds were fully comparable with that of commercial, non-environmentally degradable glue formulations for hot-melt applications.

Example 4

[0092] 800g of 88% L-Lactic Acid (Polymer grade PLA ex. Purac) solution is placed with 1.6g (0.2 wt%) Tin II chloride (Acros) powder into a 1 L pear shaped flask. The flask is attached to a rotary evaporator unit (IKA). An argon purge tube is mounted in the rotary evaporator unit so it rests just below the surface of the lactic acid solution in the flask.

An oil bath is set to 180°C and raised until the pear shaped flask is partially immersed. The vacuum pump attached to the rotary evaporator unit is set to 800 millibar for 1 to 2 hours. The argon is bubbled through the lactic acid solution. The Tin (II) oxide has easily dissolved at 180°C. The liquid will change gradually from a hazy clear solution to a crystal clear solution. The vacuum is gradually increased over the next hour to 100 millibar and the argon also subsequently reduced. After this second hour, the argon flow is stopped and the vacuum increased (or pressure reduced) to the maximum amount (5-10 millibar) and the polycondensation reaction continued for 7 hours. After this time, the vacuum is released by increasing the flow of argon and increasing the vacuum control setting to atmospheric pressure. 150 g of a 4000 Mn polycaprolactone diol (CAPA 240 ex. Solvay) and 12 g of 1,2,3-Benzenetricarboxylic anhydride, 97% (ex. Aldrich) is added to the pear shaped flask after it is removed from the rotary evaporator unit. The vacuum is again set to its maximum value, the oil bath temperature raised to 200°C and the polycondensation reaction allowed to take place for 4 hours. The final product is a slightly yellow liquid, which upon cooling to room temperature is a flexible solid and has a Mw of 12,400, a Tg of -5°C and a Tm of 120°C.

[0093] The following equipment was used in this example:

- * IKA rotary evaporator RV06-ML 2-B
- * IKA oil bath HBR 4 digital
- * Vacuubrand vacuum pump PC 2004 vario, MD 4C
- * Vacuubrand PID vacuum regulator.

Composition:	
PGLLA-88 (88%) :	800.0 g
Tin (II) chloride :	1.6 g
Capa 240 :	160.0 g
1,2,3-Benzenetricarboxylic anhydride	12.0 g

"water production" during the polycondensation of 800 g Lactic-acid:

*from the 88% PGLLA	108.0 g
*reaction water	156.2 g
total	264.2 g

[0094] Compared to example 1 more caprolactone is added which results in a larger excess of hydroxyl groups. The molecular weight that can theoretically be reached is thus lower.

[0095] In the table below the effect on the theoretical molecular weight is shown (the theoretical Mn is reached when all carboxylic groups have reacted):

Percentage capa	14.5%	17.5%	20.0%
Amount of capa	108 g	135 g	160 g
Amount of PLA	636 g	636 g	636 g
Excess of hydroxyl	0.054 eq	0.068 eq	0.080 eq
Hydroxyl Value	4.07 mgKOH/g	4.91 mgKOH/g	5.64 mgKOH/g
Mn (theoretical)	55000 g/mol	46000 g/mol	40000 g/mol

[0096] The lower molecular weight will have a negative effect on the flexibility. To avoid this the formulation can be compensated with an extra amount of di, tri or tetra acid (or excess to make the polymer carboxylic functional).

[0097] In this example an amount of 1,2,3-Benzenetricarboxylic anhydride is added to the composition. The flexibility and toughness has improved dramatically compared to formulations where no extra acid is added. The increasing flexibility shows even at low molecular weights.

[0098] The product can be used as a hot melt adhesive. Trying to separate two pieces of cardboard after they are adhered together results in cardboard tear, which means that the adhesive is stronger than the cardboard. By using a slightly higher percentage of caprolactone in the formulation the open time has improved. Even at lower temperatures this adhesive remains its flexibility. The product can also be used as a coating. After hot spraying a flexible non sticky water-resistant coating will be formed. The product is compostable.

Claims

1. Environmentally degradable polymeric compound, suitable for use as a hot melt base resin, which compound comprises 50 to 99 wt.% polylactic acid comprising chains, each of said chains having a molecular weight (Mw) of from 500 to 50 000 g/mol, to which chains a flexibilizing aliphatic polyester having a molecular weight of from 200 to 50 000 g/mol, is coupled, wherein the amount of aliphatic polyester in the compound is 1 to 50 wt.%.
5
2. Compound according to claim 1, wherein the molecular weight of said polylactic acid chains is from 1500 to 10 000 g/mol.
10
3. Compound according to any of the previous claims, wherein the molecular weight of said flexibilizing aliphatic polyester is from 1000 to 10 000 g/mol.
4. Compound according to any of the previous claims, wherein the amount of flexibilizing aliphatic polyester is from 10 to 30 wt.%.
15
5. Compound according to any of the previous claims, wherein said flexibilizing aliphatic polyester is a polymer or copolymer of hydroxycarboxylic acids, optionally substituted with hydroxy groups.
6. Compound according to any of the previous claims, wherein said flexibilizing aliphatic polyester is polycaprolactone diol, polycaprolactone triol or polycaprolactone tetrol.
20
7. Compound according to any of the previous claims, wherein said polylactic acid comprising groups are at least partially crosslinked, preferably by using an organic peroxide.
25
8. Compound according to any of the previous claims, which compound has a total molecular weight (Mw) of from 700-100 000 g/mol, preferably from 2000-50 000 g/mol.
9. Method for producing a polymeric compound, suitable for use as a hot melt base resin, comprising the steps of providing a lactic acid comprising polymer and coupling said lactic acid comprising polymer to a flexibilizing aliphatic polyester under condensation and/or transesterification reaction conditions.
30
10. Method according to claim 9, wherein said condensation and/or transesterification reaction conditions comprise the contacting with a catalyst, which catalyst comprises at least one metal selected from antimony, tin (II), tin (IV), iron (II), iron (III), zinc, calcium, magnesium, transition metals and rare earth metals; optionally in combination with an acidic catalysts selected from sulfuric acid, phosphoric acid, hydrochloric acid, methanesulfonic acid, and/or toluene sulfonic acid.
35
11. Method according to claim 10, wherein said catalyst is stannous oxide, stannous chloride, stannous lactate, stannous 2-ethylhexanoate and/or zinc lactate.
40
12. Method for producing a polymeric compound, suitable for use as a hot melt base resin, comprising the steps of providing a lactic acid comprising polymer and coupling said lactic acid comprising polymer to a "flexibilizing" aliphatic polyester with the use of coupling agents.
45
13. Method according to claim 12, wherein said coupling agent is a cyclic anhydride, a di-, tri- or tetra-cyclic anhydride, a polyanhydride, a cyclic or glycidal ether, an aliphatic isocyanate, an aliphatic polyisocyanate, a silane and/or a chlorosilane.
14. Use of a compound as described by any of the previous claims as an impact modifier for high molecular weight polylactide resins or copolymers of polylactic acid and polyglycolic acid; a hot melt adhesive; a hot melt coating; a hot melt castable film; a hot melt castable fiber; or a melt blown nonwoven.
50
15. End use product comprising a hot melt base resin according to any of the claims 1-8 or a hot melt base resin obtained by the method of any of the claims 9-13.
55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 20 0800

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 399 666 A (FORD THOMAS M) 21 March 1995 (1995-03-21) * column 3, line 1-32; claims 1,2,5; examples 2-4,6-9 *	1-6,8,15	C08G63/08 C08G63/78 C08L67/04 C08L67/02
X	PENCO M ET AL: "Thermal properties of a new class of block copolymers based on segments of poly(d,l-lactic-glycolic acid) and poly(ε-caprolactone)" EUROPEAN POLYMER JOURNAL, PERGAMON PRESS LTD. OXFORD, GB, vol. 36, no. 5, May 2000 (2000-05), pages 901-908, XP004189889 ISSN: 0014-3057 * table 1 *	1-6,8	
X	US 5 028 667 A (DRYSDALE NEVILLE E ET AL) 2 July 1991 (1991-07-02) * example 7 *	1,2,4-6,8	
X	DE 43 00 420 A (BASF AG) 14 July 1994 (1994-07-14) * page 3, line 62 - page 3, line 66; claims 1-3,5,6; example 2 *	1-6,8-11	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C08G C08L
X	EP 0 765 913 A (DAINIPPON INK & CHEMICALS) 2 April 1997 (1997-04-02) column 14, lines 18-36 column 22, lines 10-37 * examples 13,14 *	9-11	
X	US 5 646 217 A (HAMMOND TIMOTHY) 8 July 1997 (1997-07-08) * claim 1; example 4 *	9-11	
-/--			
-The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 20 November 2001	Examiner Rousseau, F
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (03/02) (P4/C01)



European Patent
Office

LACK OF UNITY OF INVENTION
SHEET B

Application Number

EP 01 20 0800

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-6, 8(part), 14 (part), 15 (part)

Subject-matter related to polymers defined according to claims 1-6, wherein the polylactic acid comprising chains are not crosslinked and their use for hot melt applications.

2. Claims: 7, 8(part), 15(part)

Subject-matter related to polymers defined according to claims 1-6, wherein the polylactic acid comprising chains are at least partially crosslinked and their use for hot melt applications.

3. Claims: 9-11

Method according to claims 9-11

4. Claims: 12-13

Method according to claims 12-13

5. Claim : 14(part)

Use of the compounds defined in claims 1-8 as impact modifier for high molecular weight polylactide resins or copolymers of polylactic acid and polyglycolic acid.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 20 0800

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 992 529 A (UNITED STATES SURGICAL CORP) 12 April 2000 (2000-04-12) * page 3, line 11 - page 3, line 21; claims 1,2 *	9-11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 20 November 2001	Examiner Rousseau, F
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (3.92) (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 01 20 0800

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-11-2001

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5399666	A	21-03-1995	AU	1988395 A	16-11-1995
			CA	2187625 A1	02-11-1995
			CN	1146775 A	02-04-1997
			EP	0756608 A1	05-02-1997
			FI	964217 A	18-10-1996
			JP	9512571 T	16-12-1997
			WO	9529200 A1	02-11-1995

US 5028667	A	02-07-1991	AT	124709 T	15-07-1995
			AU	6624490 A	28-04-1991
			BR	9007686 A	18-08-1992
			CA	2066029 A1	30-03-1991
			CN	1051367 A	15-05-1991
			DE	69020739 D1	10-08-1995
			DE	69020739 T2	23-11-1995
			EP	0493529 A1	08-07-1992
			FI	921351 A	27-03-1992
			GR	90100721 A	20-01-1992
			IE	903483 A1	10-04-1991
			JP	2858947 B2	17-02-1999
			JP	5500982 T	25-02-1993
			MX	22628 A	01-11-1993
			NO	921190 A	26-03-1992
			NZ	235503 A	26-03-1993
			PL	287107 A1	23-03-1992
			PT	95470 A	22-05-1991
			WO	9105001 A1	18-04-1991
			US	5095098 A	10-03-1992
			ZA	9007797 A	27-05-1992

DE 4300420	A	14-07-1994	DE	4300420 A1	14-07-1994

EP 0765913	A	02-04-1997	JP	9095603 A	08-04-1997
			JP	9104809 A	22-04-1997
			EP	0765913 A1	02-04-1997
			US	5686540 A	11-11-1997

US 5646217	A	08-07-1997	AU	674361 B2	19-12-1996
			AU	5426894 A	08-06-1994
			CA	2147857 A1	26-05-1994
			EP	0669959 A1	06-09-1995
			FI	952162 A	05-05-1995
			WO	9411440 A2	26-05-1994
			JP	8503500 T	16-04-1996
			NO	951766 A	05-05-1995

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 20 0800

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The annexes are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-11-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0992529 A	12-04-2000	EP US	12-04-2000
		0992529 A2 6287499 B1	11-09-2001

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82